Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 2501–2504

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

High DC resistivity in microwave sintered $Li_{0.49}Zn_{0.02}Mn_{0.06}Fe_{2.43}O_4$ ferrites

Parveen Kumar[a], J.K. Juneja[b,*], Chandra Prakash[c], Sangeeta Singh[d], Ravi K. Shukla[e], K.K. Raina[e]

[a]*Electroceramics Research Lab, GVM Girls College, Sonepat, Haryana 131001, India*
[b]*Department of Physics, Hindu College, Sonepat, Haryana 131001, India*
[c]*Solid State Physics Laboratory Lucknow Road, Delhi 110054, India*
[d]*Department of Physics, GVM Girls College, Sonepat, Haryana 131001, India*
[e]*School of Physics & Material Science, Thapar University, Patiala 147004, India*

Received 14 June 2013; received in revised form 13 July 2013; accepted 13 July 2013
Available online 20 July 2013

Abstract

Ferrites with compositional formula $Li_{0.49}Zn_{0.02}Mn_{0.06}Fe_{2.43}O_4$ were prepared by solid state reaction route and were sintered using conventional and microwave furnaces. The structural and electrical properties were studied and compared. Dielectric constant and tanδ were measured as a function of temperature and frequency. DC resistivity of the samples was calculated by impedance analysis in the temperature range from 25 °C to 150 °C. High DC resistivity (10k–100 kΩ m) was observed for microwave sintered ferrite sample as compared to conventionally sintered sample (2–80 Ω m) in the measured temperature range.

Keywords: A. Sintering; C. Dielectric properties; C. Electrical properties; D. Ferrites

1. Introduction

Lithium and substituted lithium ferrites have been found to be excellent alternative for garnets in microwave devices due to their low costs, high resistivity and low eddy current losses. For device applications, physical properties of lithium ferrites can be tailored by substituting them with different metal ions such as Cd^{2+}, Cu^{2+}, Co^{2+}, Ti^{4+}, Mg^{2+}, Al^{3+}, Mn^{4+}, Zr^{4+}, Gd^{3+} etc. Dielectric properties of substituted lithium ferrite depend on factors like the method of preparation, substitution of different cations, etc. There are many techniques to synthesize ferrites but due to its time and energy saving advantage, microwave sintering is the most popular among all the novel techniques. Microwave sintering can result in synthesis of ferrites with high density and uniform microstructure [1–6]. Lithium ferrite samples, prepared by microwave sintering not only show the improvement in their physical properties like density and microstructure but they also show the improvement in their electrical and magnetic properties. In the present paper we are reporting the various improvements observed in the structural and electrical properties of the microwave sintered (MS) ferrites in comparison to conventionally sintered (CS) ferrites.

2. Experimental

Zn–Mn substituted Li-ferrites with compositional formula $Li_{0.49}Zn_{0.02}Mn_{0.06}Fe_{2.43}O_4$ were prepared by conventional solid state reaction route and then were pressed into circular pellets and finally these pellets were sintered conventionally and by using microwave furnace [7]. Pellets were sintered at 1050 °C for 2 h using conventional furnace (at the rate of 5 °C/min) and at 1050 °C for 10 min using microwave furnace (at the rate of 50 °C/min). For microwave sintering the pellets were kept in alumina chamber along with succeptors. The chamber was then kept inside the microwave cavity (2.45 GHz) of the furnace. Dielectric constant 'ε' and tanδ were measured as a function of temperature (25–150 °C) and frequency (70 Hz–1 MHz). Complex impedance 'Z^*' was

*Corresponding author. Tel.: +91 9416260242.
E-mail address: jk_juneja@yahoo.com (J.K. Juneja).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.07.063

calculated using the observed values of ε and tanδ. DC resistivity was calculated from the X-axis intercepts of Cole–Cole plots for Z^*.

3. Results and discussion

Cu-K_α ($\lambda = 1.54$ Å) radiations were used for X-ray diffraction (XRD) analysis. XRD patterns for both CS and MS samples are shown in Fig. 1. Both samples exhibit single cubic spinel phase with space group symmetry *Fd3m*. The pattern is indexed by using Rietveld method and the lattice constant is found to be 8.31299 Å (CS) and 8.33674 Å (MS). SEM images for both the samples are given in the insets of Fig. 2. Finer grains (~0.7 μm) are observed in MS sample as compared to CS sample (~15 μm). The ρ–T curves for CS and MS samples are shown in Fig. 2. The resistivity is calculated from the resistance given by the X axis intercepts of the Cole–Cole plot for Z^*. High value of ρ~10 kΩ m at 150 °C and ~100 kΩ m at 25 °C is observed in MS sample whereas in case in CS sample it is less than 80 Ω m. The variation of ε and tanδ as a function of frequency at 25 °C for CS and MS ferrite samples is shown in Fig. 3. Both ε and tanδ show a decreasing trend with increase in frequency, with the exception that there is except only a small increase in tanδ beyond 100 kHz in case of CS sample which may be due to some external factors. The decrease in ε with increase in frequency is due to the fact that at lower frequencies all types of polarizations like electronic, ionic, dipolar and interfacial polarization are present resulting in high ε is high but at higher frequencies the contribution from the bigger dipoles decreases which cannot oscillate with frequently changing field and only electronic polarization contributes to the dielectric polarization. MS sample shows small value of tanδ as compared to CS sample.

The value of ε decreases rapidly with frequency in case of CS sample as compared to MS sample. The value of ε of polycrystalline ferrite ceramics is additionally affected by microstructure, grain size, density, DC resistivity and impurities present in the sample. The dependence of ε on grain size is explained by the Maxwell–Wagner effect. As main contribution to the dielectric constant at higher frequencies is due to the atomic and electronic polarization hence the value of ε is of the same order for both the samples. In case of ferrites, the DC resistivity plays a vital role in dielectric polarization. Both ε and DC resistivity are double-side affected by porosity (density). Close pores (inside grains or at grain boundaries) will reduce ε because of the unit dielectric constant of air (pores). Open (interconnected) pores, in case of absorbing impurities (e.g. water) may increase dielectric constant,

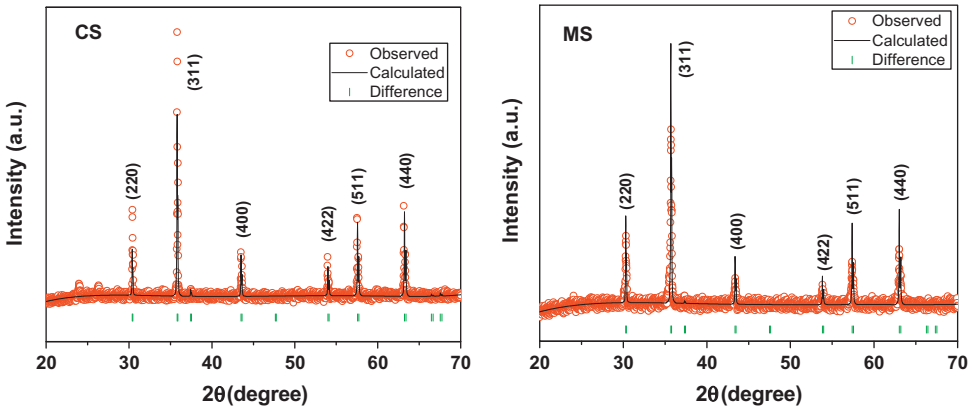

Fig. 1. Observed (circles) and calculated (solid lines) X-ray diffraction pattern for both samples and indexed by using the Rietveld method (with space group symmetry *Fd3m*).

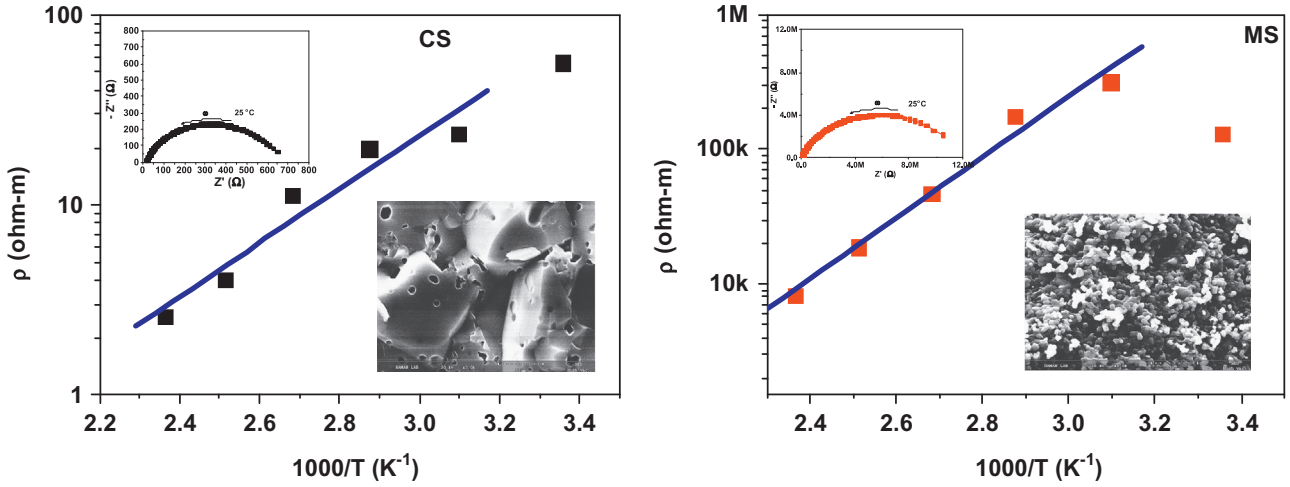

Fig. 2. The linear fits of ρ–T curves for both CS and MS samples (inset showing SEM and semicircular fits of complex Cole–Cole plots at 25 °C).

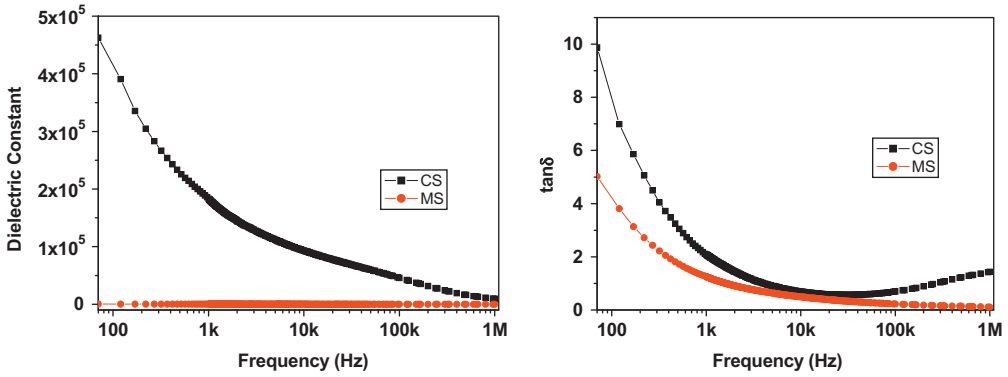

Fig. 3. Variation of ε and tanδ with frequency at room temperature.

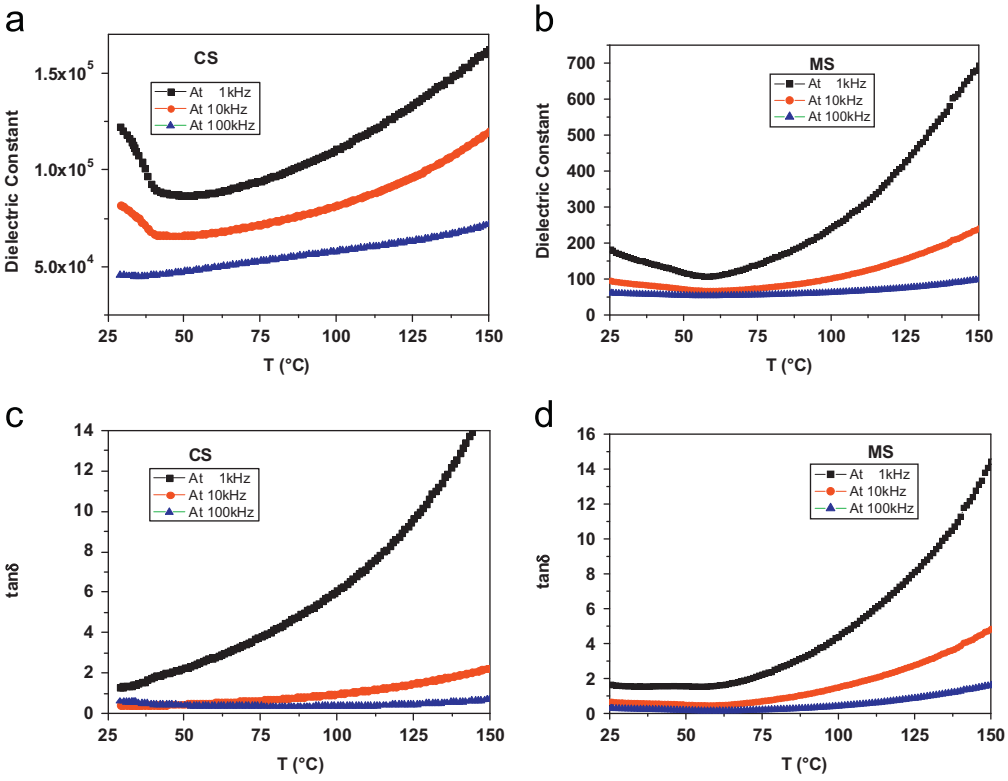

Fig. 4. Variation of ε and tanδ with temperature.

because of high permeability of water. Structural defects/imperfections could also increase polarization. Ceramic samples with uniform microstructure and high density can easily be prepared by microwave sintering [2].

In ferrites, presence of Fe^{2+} increases the polarization and thus ferrites containing a larger number of Fe^{2+} ions are likely to exhibit a higher value of ε. The high value of ε in case of ferrites is undesired because it is always accompanied by extremely high dielectric loss tangent (tanδ). In CS sample, very high value of ε as compared to ε in MS samples may be due to the presence of large amount of Fe^{2+}. This is because there is always some probability of Verwey's electron hopping between Fe^{3+} and Fe^{2+} which are randomly situated at *B*-sites. Also lithium and oxygen loss is there. The rapid and enhanced reaction process during microwave sintering may have given less opportunity for material loss and reducing the chance for formation of Fe^{2+} [8]. The variations of ε and tanδ as a function of temperature at three different frequencies (1 kHz, 10 kHz and 100 kHz) for both the samples are shown in Fig. 4. It is also observed that for both the samples, ε increases with increase in temperature, but beyond a certain temperature it increases rapidly. This increase in ε shows the dominance of space charge (interfacial) polarization. Also with increase in temperature, thermal activation of the electric charge carriers increases their number and drift velocity and thus the dielectric constant [9]. Further it can be noticed that at all the frequencies, the rise in ε with temperature is more pronounced and the rapid rise starts at much lower temperature in CS sample. Higher electrical resistivity in MS sample offers greater resistance to thermal activation of the polarizable charges thus delaying polarization.

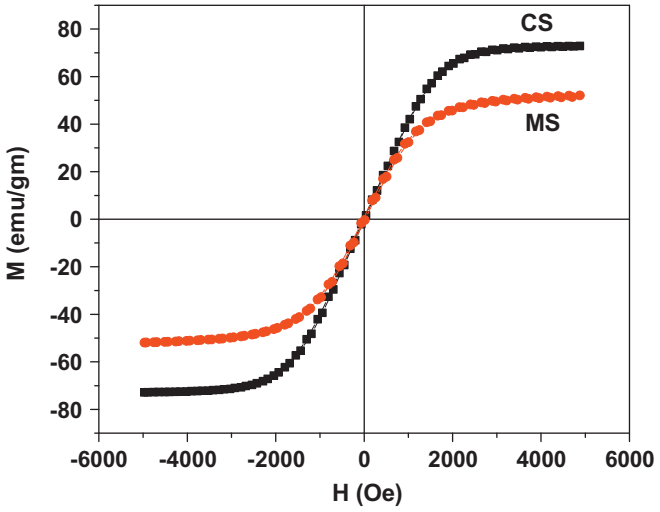

Fig. 5. M–H loops of both samples at 25 °C.

Hence the rise in dielectric constant with temperature is comparatively slow at low temperature and rapid at higher temperatures. Thus it is clear that the MS sample shows better temperature stability. The initial decrease in ε with temperatures may be due to presence of some external reasons. As ε and resistivity are roughly inversely proportional in ferrites, small value of tanδ can be observed in MS sample. However its value increases as temperature increases, which may be due to the increase in the conduction with temperature [10,11]. Fig. 5 shows the saturated M–H loops at 25 °C for both CS and MS samples. Saturation magnetization 'M_{sat}' for MS sample is 50 emu/g whereas in CS sample is 72 emu/g. This difference in M_{sat} value for both the samples may be due to presence of different amounts of Fe^{3+} (diamagnetic) and Fe^{2+} (paramagnetic) ions [12].

4. Conclusion

Single phase Zn–Mn substituted lithium ferrite samples with improved properties can be prepared by using microwave sintering technique. High DC resistivity in case of ferrite samples prepared by microwave sintering can be attributed to the limited electron hopping between Fe^{3+} and Fe^{2+}. The greater thermal stability of dielectric constant in the microwave sintered samples as compared to conventionally sintered ferrite sample can be attributed to the formation of finer grains.

References

[1] J. Smith, H.P.J. Wijin, Philips Technical Library (1969).
[2] S.R. Murthy, Development of low-power loss Mn–Zn ferrites using microwave sintering method, Bulletin of Materials Science 26 (2003) 499.
[3] M. Maisnam, S. Phanjoubam, H.N.K. Sharma, C. Prakash, L. Radhapiyari Devi, O.P. Thakur, Magentic properties of vanadium-substituted lithium zinc titanium ferrite, Materials Letters 58 (2004) 2412.
[4] M.A. Ahmed, N. Okasha, A. Ebrahem, Correlation of the physic chemical properties of Zn-substituted Li–La ferrite, Ceramics International 31 (2005) 361.
[5] U.B. Shinde, S.E. Shirsath, S.M. Patange, S.P. Jadhav, K.M. Jadhav, V.L. Patil, Prepartion and characterization of Co^{2+} substituted Li–Dy ferrite ceramics, Ceramics International 39 (2013) 5227.
[6] Y.C. Venudhar, K.S. Mohan, Dielectric behavior of lithium–cobalt mixed ferrites, Materials Letters 54 (2002) 135.
[7] M. Maisnam, S. Phanjoubam, P. Kumar, J.K. Juneja, A. Kumar, C. Prakash, Improved properties of Li–Mn–Ti ferrites by microwave sintering, Integrated Ferroelectrics 122 (2010) 31.
[8] E.J.W. Verwey, J.M. De Boer, Cation arrangement in a few oxides with crystal structures of the spinel type, Recueil des Travaux Chimiques des Pays-Bas 55 (1936) 531.
[9] L.L. Hench, J.K. West, Principles of Electroceramics, John Wiley & Sons, New York, 1990.
[10] S.K. Pandey, A.R. James, Chandra Prakash, T.C. Goel, K. Zimik, Structural, dielectric and magnetic properties of NiCuZn ferrite grown by citerate precursor method, Materials Science and Engineering B 133 (2006) 42.
[11] D. Ravinder, A.C. Reddy, Dielectric properties of Li–Ge ferrites, Materials Letters 57 (2003) 2855.
[12] P. Yadoji, R. Peelamedu, D. Agrawal, R. Roy, Microwave sintering of Ni–Zn ferrites: comparison with conventional sintering, Materials Science and Engineering B 98 (2003) 269.